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Kinetic and Electrical Conductivity Measurement Study of SDBF Resin

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Abstract:

Resin SDBF has been synthesized by the condensation of salicylicacid and diaminobenzoicacid with formaldehyde and hydrochloricacid as catalyst. Thermal degradation curve has been discussed which shows four decomposition steps. Detailed thermal degradation studies of the resin have been carried out to ascertain its thermal stability. Sharp–Wentworth and Freeman–Carroll methods have been used to calculate activation energies and thermal stability. The activation energy (Ea) calculated by using the Sharp–Wentworth (17.2 kJ/mol) has been found to be in good agreement with that calculated by Freeman–Carroll (26.80 kJ/mol) method. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S*) and frequency factor (Z) have also been evaluated on the basis of the data of Freeman–Carroll method. The order of reaction (n) is found out to be 1.03. Electrical conductivity measurements have been also conceded to ascertain the semiconducting nature of the resin.

Keywords: Resin; synthesis, Thermal properties, Activation energy, Electrical conductivity.

1. INTRODUCTION

The resins offer novelty and versatility; hence they occupy the pivotal position in the field of material science. The progress in the field resins has been extremely rapid, as they generally useful in packaging, adhesives and coatings in electrical sensors and organometallic semiconductors [1-4]. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties [5-7].Various researchers have been studied the applications of resins of substituted phenols and formaldehyde [8-10]. 2-Hydroxyaceto phenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabilizers. Resins of salicylic acid, thiourea with trioxane and p-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [11-15].

Semiconductors are the most important ingredients of modern electronics. The concerted research effort was carried out to aim at developing an organic material that would posses the good electrical properties as the inorganic semiconductors. In the early days the prime attention was placed on the synthesis of highly conductive polymers, preferably of high molecular weight and the measurement of their electronic conductivity properties i.e. conductivity, mobility, thermoelectronic power, etc. The resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low [16-18]. Kand a et al reported the rubeanato –copper semiconductive polymers and studied their AC and DC conductivity [19]. Dhawan and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting diodes, antistatic and EMI materials, sensors, opto- electronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [20].

In our laboratory, study on the synthesis of materials for high thermal stability and electrical conductivity measurements of resins derived from salicylicacid / p-hydroxybenzoicacid, diamide / urea / thiourea with formaldehyde [6, 7, 12-14, 21-24]. The present communication deals with thermal degradation and electrical conductivity properties of a newly synthesized resin derived from salicylicacid, diaminobenzoicacid and formaldehyde.

Methods for the estimation of kinetic parameters from thermo gravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible. After treating the thermal degradation data with Sharp–Wentworth (SW) and Freeman– Carroll (FC) methods, activation energy and kinetic parameters such as ΔF, ΔS, Z, S* and n (order of reaction) have been evaluated [25-27]. For the electrical conductivity measurement study the DC resistivity of the SDBF resin have been measured by applying a constant voltage (50 volts) across the pellets. The

temperature dependence of the electrical conductivity of the resin has been plotted. The energy of activation (E_a) of electrical conduction is calculated from the slope of the plots. Electrical conductivity of the resin has been studied with increase in temperature.

2. EXPERIMENTAL

2.1 Chemicals

All Chemicals were AR grade. Salicylicacid, diaminobenzoicacid and formaldehyde were purchased from Aldrich Chemical Co., USA. DMF and DMSO were used as solvent of HPLC grade.

2.2 Instruments Used

Thermogravimetric analyses (TGA) of resin sample has been carried out by using Perkins Elmer TGS-ll thermal analyzer at heating rate of 10^0C per minute and in air atmosphere upto 800^0C. The thermogram was recorded at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujrat.

The electrical resistivity of the resin was measured with help of Hewlett-Packard 4192 Impendance Analyser 5Hz-13MHz at Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur over a wide range of temperature i.e. from 313-423 K.

2.3 Synthesis and Characterization of SDBF Resin

A mixture of salicylicacid, diaminobenzoicacid and formaldehyde was taken in the ratio of 1: 1: 2 with 2 mol–L^{-1} hydrochloricacid as catalyst in a round bottom flask. The flask was fitted with water condenser and heated in an oil bath at 120^0C for 7 hours with occasional shaking. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified. The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agated mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air-dried powder was extracted with diethyl ether and followed by washing with the petroleum ether to remove salicylicacid - diaminobenzoicacid copolymer, which might be present along with SDBF resin.

n Salicylic acid + n Diaminobenzoic acid + 2n HCHO (Formaldehyde) —(2M HCl, 120^0C)→ SDBF Resin + 2n H_2O

Scheme: Synthesis of SDBF Resin

3. THERMOGRAVIMETRY

Thermal analysis method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA the sample is subjected to conditions increase in temperature at linear rate [28, 29].

Freeman–Carroll and Sharp- Wentworth methods have been employed for the calculation of kinetic parameters of the newly synthesized resin with help of dynamic TG curve [6,12,14,22-24,27]. The advantage of Freeman and Carroll method that in one single stage by keeping heating rate constant both the order of reaction and energy of activation can calculated in a single experiment. The following expression is used to evaluate various kinetic parameters:

$$\frac{\Delta \log dw/dt}{\Delta \log Wr} = n - \frac{Ea}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log Wr}$$

Hence, a plot of $\frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log W_r}$ vs. $\frac{\Delta(1/T)}{\Delta \log W_r}$ should give a straight line with an intercept on y-axis equal to the value of n (the order of reaction) and the slope m = E / 2.303R.

Where, dw/dt is the rate of change of weight with time and in expression Wr = Wc –w,

W_c is the weight loss at the completion of the reaction, w is the total weight loss upto the time t and T is the temperature in k.

The following expression is used to evaluate Ea with Sharp-Wentworth method:

$$\log \frac{(dc/dT)}{(1-c)} = \log(A/\beta) - \left[\frac{E_a}{2.303R}\right] \cdot \frac{1}{T}$$

Where, dc/dt is the rate of change of mass with time t, T is the temperature and β= ΔT/dt.

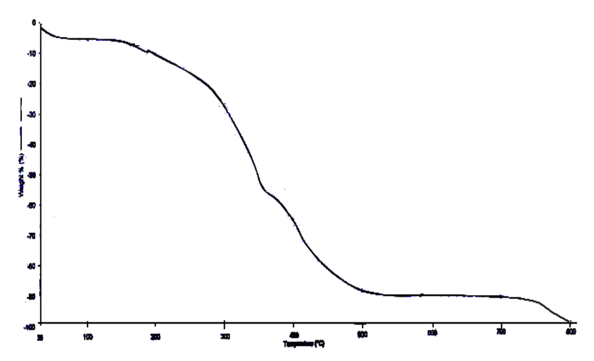


Fig.1: Thermogram of SDBF resin

4. ELECTRICAL CONDUCTIVITY

The resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low. This is due to the difficulty which electrons experience in jumping from one molecule to another and so the carrier mobility in compounds of these kind increases with increase in molecular size [16-20].The measurements involved following steps.

4.1 Preparation of pellets for Resistance Measurements

Resin was dried and thoroughly ground in agate pestle and mortar to palatalized isostatically in a steel die at 10 tones/2inch with the help of hydraulic press. A thin layer of colloidal graphite in acetone was applied on both sides of the pellets and dried at room temperature for 4-6 hr. The colloidal graphite on either side of pellets functioned as electrode. The surface continuity of pellet was then tested by means of mutlimeter. The average diameter of this pellets and its thickness were measured using Screw Gauze. Actual dimensions were measured as average of the three measurements taken at three places.

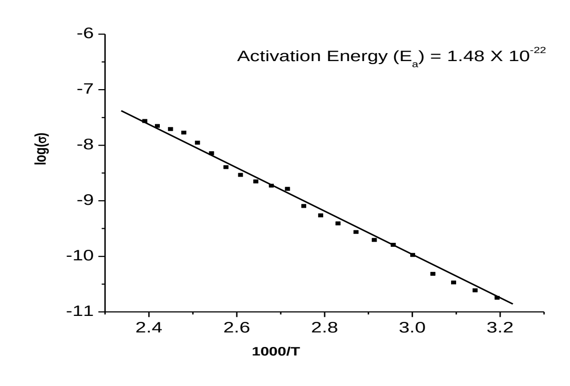


Fig.2: Electrical Conductivity Plot of SDBF Resin

4.2 Measurement of Resistivity

Hewlett-Packard 4192 Impendance Analyser 5Hz-13MHz was used to measure the electrical conductivity of all resin. The temperature variations of resin were studied by placing the sample holder along with the pallet in the electric furnace and were then heated slowly. The slow rate of heating 1 to 10 ^{0}C per minute was maintained throughout the investigation. Connection wires from the furnace were connected to the terminals of the instrument. The resistances of the sample pallets were measured by two probes (terminals) method.

Resistivity (ρ) was then calculated using the relation:

$$\rho = R. \times A/l$$

Where, R= resistance of the pellet.

A = Surface area of pellets and

l = Thickness of pellet.

The DC resistivities were measured from 313 to 423 K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship.

$$\sigma = \sigma_0 \exp^{-Ea/kT}$$

Where, σ =electrical conductivity at room temperature (T)

σ_0 =electrical conductivity at temperature constant

Ea =Activation energy of electrical conduction.

K= Boltazmann constant (1.3817x10-23 J mole^{-1}k^{-1})

T= Absolute temperature

The relationship has been modified as

$$\text{Log } \sigma = \log\sigma_0 + \ -Ea/2.303kT$$

According to this relation, a plot of Log σ Vs 1/T would be linear with negative slope. From the Slope of the plots, the activation energy was calculated [16-20, 31].

5. RESULTS AND DISCUSSION

5.1 Thermal Degradation Study for SDBF Resin

The thermal degradation curve for SDBF resin is shown in Figure1 exhibits four-stage decomposition. First stage was slow and ranged from 40-160^{o}C corresponding to loss 5.6% which may be due to entrapped H_2O molecule. The second stage decomposition represents loss of side chain attached to aromatic nucleus and-OH group.[Obs.60.0% againstcalc.59.59%].The third stage decomposition at 240-420 ^{o}C which may be due to the loss of -COOH group [observed 78.2% and calculated 77.7%]. The fourth state decomposition is probably total decomposition of resin. The Half Decomposition temperature for SDBF resin is found to be 225^{o}C.

By using thermal decomposition data and then applying the Sharp-Wentworth method activation energy has been calculated which is in agreement with the activation energy calculated by Freeman-Carroll method. The thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are incorporated in [Table-1].

Due to abnormally low value of frequency factor [Z] it may be classified as a slow reaction and no other obvious reason can be given. The value of entropy [ΔS] indicates that the activated polymer has more ordered structure than the reactants and the reaction are slower than normal. This is

further supported by low Z values [22- 24, 28, 29].It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [Ea] as decomposition mechanism is expected to be complicated. Positive values of activation energy under present investigation correspond to the energy of activation due oxidation–reduction process of resin in the higher temperature range [22- 24, 28, 29].

Fairly straight line plots are obtained using the two methods. However, using the Freeman- Carroll method some abnormal points were ignored to get a clear picture about most of the points. Similarly, in the Sharp- Wentworth method, some points at the beginning or the end did not fall on straight line. This is expected, since, the decomposition of resin is not obeying first order kinetics perfectly. These observations are in harmony with the findings of Jacobs and Tompkin and other earlier workers [30].

5.2 Electrical Conductivity for SDBF Resin

The results of electrical conductivity and activation energy are incorporated in Table2. The temperature dependence of the electrical conductivity of the resin has been mentioned in Fig.2.The electrical conduction of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation, atmosphere etc; activation energy (Ea) is not affected by these parameters and, therefore, it is fairly reproducible [31-35]. The magnitude of activation energy depends on the number of electrons present in semiconductor materials. The more the number of Л – electrons lowers the magnitude of activation energy and vice versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those with aliphatic system. Thus, the low magnitude of activation energy may be due to the presence of large number of Л-electrons in the polymer chain. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [16-20, 31-35].The carrier motilities of the organic semiconductors might decrease due to:

A. The forces between the adjacent molecules are relatively weak as organic compounds from molecular crystals.
B. Due to little electronic coupling that exists between the adjacent molecules, it becomes difficult for the electrons to jump from one molecule to other.
C. As a consequence of the disordered structure which is due to amorphous nature, the electrons get scattered while traveling through the materials, when they try to flow through it and hence lowers the conductivity.

The study shows following results of electrical conductivity-

1) The electrical conductivity of SDBF resin lies in the range of 1.74×10^{-11} to 1.22×10^{-7} Siemen.

2) The plots of log σ versus 1/T is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma o \exp(\Delta E/kT)$ is obeyed.

3) The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots is found to be in the range of 1.48×10^{-22} J/K.

These observations and results are in harmony with the findings of other earlier workers [16-20, 34, 35]

6. CONCLUSION

Thermogram of the resin depicts four stages of decomposition. The observed weight loss is little higher than the calculated. This may be due to the degradation of side chain of resin. Activation energy by both Sharp-Wentworth and Freeman-Carroll method are in good agreement with each other. Low value of frequency factor [Z] it may be concluded that the reaction of decomposition of resin can be classified as a slow reaction. The negative values for entropy indicate that the activated polymer has more ordered structure than the reactants which are further supported by low Z value. The decomposition of resin is following first order kinetics although not perfectly.

Electrical conductivity of this resin increases with increase in temperature which is the important property essential for the resin may be ranked as semiconductors. Hence, this new polymer may be semiconducting in nature.

7. AKNOWLEDGEMENT

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Table1: Result of thermogravimetric analysis of SDBFresin

Decom-position Temp. (T)	Half Decom-position Temp. (T*)	Activation Energy kJ/mole		Kinetic parameters by FC				
		Freeman-Carroll FC	Sharp-Wentworth SW	Entropy change ΔS(J)	Free energy change ΔF(kJ)	frequency factor Z (S^{-1})	Apparent entropy S*(J)	n
282	499	26.80	17.2	8.3	22.66	994.52	-22.78	1.03

Table 2: Evaluation of Activation Energy of Conduction SDBF Resin

Diameter of the pellet = 1.287
Surface area of the pellet (A) = $\pi r^2 = 3.142 \times (0.643)^2 = 1.301\ cm^2$
Thickness of pellet (l) = 0.196 cm.
A/l = 6.995 cm.

Temp (K)	1000/T (K^{-1})	Resistance in Ohm 'R'	Resistivity p = RA/l (Ohm.cm)	Electrical Conductivity σ = 1/ρ (Siemen.cm^{-1})	Logσ
313	3.1949	8.65×10^9	5.74×10^{10}	1.74×10^{-11}	-10.7590
318	3.1447	6.33×10^9	4.20×10^{10}	2.38×10^{-11}	-10.6234
323	3.0960	4.59×10^9	3.05×10^{10}	3.28×10^{-11}	-10.4838
328	3.0488	3.21×10^9	2.13×10^{10}	4.69×10^{-11}	-10.3285
333	3.0030	1.46×10^9	9.69×10^9	1.03×10^{-10}	-9.9864
338	2.9586	9.60×10^8	6.37×10^9	1.57×10^{-10}	-9.8043
343	2.9155	7.84×10^8	5.20×10^9	1.92×10^{-10}	-9.7163
348	2.8736	5.67×10^8	3.76×10^9	2.66×10^{-10}	-9.5756

353	2.8329	3.96×10^{8}	2.63×10^{9}	3.80×10^{-10}	-9.4197
358	2.7933	2.83×10^{8}	1.88×10^{9}	5.32×10^{-10}	-9.2738
363	2.7548	1.92×10^{8}	1.27×10^{9}	7.85×10^{-10}	-9.1053
368	2.7174	9.47×10^{7}	6.29×10^{8}	1.59×10^{-9}	-8.7984
373	2.6810	8.26×10^{7}	5.48×10^{8}	1.82×10^{-9}	-8.7390
378	2.6455	6.93×10^{7}	4.60×10^{8}	2.17×10^{-9}	-8.6628
383	2.6110	5.31×10^{7}	3.52×10^{8}	2.84×10^{-9}	-8.5471
388	2.5773	3.84×10^{7}	2.55×10^{8}	3.92×10^{-9}	-8.4064
393	2.5445	2.16×10^{7}	1.43×10^{8}	6.97×10^{-9}	-8.1565
398	2.5126	1.39×10^{7}	9.23×10^{7}	1.08×10^{-8}	-7.9650
403	2.4814	9.17×10^{6}	6.09×10^{7}	1.64×10^{-8}	-7.7844
408	2.4510	7.92×10^{6}	5.26×10^{7}	1.90×10^{-8}	-7.7207
413	2.4213	4.40×10^{6}	2.92×10^{7}	3.42×10^{-8}	-7.4655
418	2.3923	2.83×10^{6}	1.88×10^{7}	5.32×10^{-8}	-7.2738
423	2.3641	1.23×10^{6}	8.16×10^{6}	1.22×10^{-7}	-6.9119